NICKEL AND COMPOUNDS

Nickel and nickel compounds were identified as a toxic air contaminants under California's air toxics program (AB 1807) in 1991.

CAS Registry Number: nickel = 7440-02-0 Ni
nickel carbonyl = 13463-39-3 $Ni(CO)_4$

Molecular Formula: nickel = Ni
nickel carbonyl = C_4NiO_4

Nickel is an odorless, silvery, dark gray metal which crystallizes with a face-centered cubic structure. It is insoluble in water and ammonia, soluble in dilute nitric acid, and is more resistant to atmospheric and aqueous corrosion than iron and cobalt. Nickel retains a high polish, is highly ductile, and has good thermal and electrical conductivity (Merck, 1989; HSDB, 1995).

Nickel carbonyl (nickel tetracarbonyl) is a colorless, volatile liquid at room temperature, boiling at 43 °C and it explodes at 60 °C. It is soluble in alcohol, benzene, chloroform, acetone, and carbon tetrachloride (Merck, 1989). See Table I for physical properties of some nickel compounds.

Physical Characteristics of Nickel

Atomic Weight:	58.71
Atomic Number:	28
Valences:	2 & 3
Boiling Point:	2,730 °C
Melting Point:	1,455 °C
Vapor Pressure:	1 mm at 1,810 °C
Density/Specific Gravity:	8.9

(HSDB, 1995; Merck, 1989; Sax, 1989; U.S. EPA, 1994a)

SOURCES AND EMISSIONS

A. Sources

Nickel is used for the production of various metal alloys, cast irons, and electroplated goods (ARB, 1991d). Nickel is used for manufacturing corrosion-resistant alloys, electroplating, and the production of catalysts and nickel-cadmium batteries (Proctor et al, 1988). Nickel carbonyl is

used as a purification intermediate in refining nickel; and as a catalyst in the petroleum, plastic, and rubber industries (ARB, 1991d).

Nickel has also been detected or identified in motor vehicle exhaust by the Air Resources Board (ARB) (ARB, 1995e). Fuel combustion (residential oil, distillate oil, coke and coal) is responsible for the majority of the total statewide emissions of nickel. The particles which result from combustion are typically less than 1 micrometer (μm) in diameter while large particles (greater than 10 μm) are likely to arise from wind action on soils, deposited dusts, and fugitive emissions from dust producing operations (ARB, 1991d).

The primary stationary sources that have reported emissions of nickel in California are crude oil and gas extraction, electrical services, and national security installations (ARB, 1997b).

B. Emissions

The total emissions of nickel and nickel compounds from stationary sources in California are estimated to be at least 130,000 pounds per year, based on data reported under the Air Toxics "Hot Spots" Program (AB 2588) (ARB, 1997b).

In January 1993, the Air Resources Board (ARB) adopted an airborne toxics control measure for non-ferrous metal melting operations. This control measure is expected to reduce emissions of arsenic, cadmium, and nickel by 99 percent (ARB, 1992f).

C. Natural Occurrence

Nickel's abundance in the earth's crust is 0.018 percent and it is found in many ores such as sulfides, arsenides, antimonides, and oxides or silicates. The most predominant forms are nickel sulfate and nickel oxides (U.S. EPA, 1994a). Chief sources include chalcopyrite, pyrrhotite, pentlandite, garnierite, nicolite, and millerite. Nickel and nickel compounds constitutes 0.03 percent of the particulate matter suspended in the atmosphere. Nickel occurs as nickel powders deposited as meteoritic dust from the stratosphere. Natural sources of airborne particles that contain nickel include soil, sea spray, volcanoes, forest fires, and vegetation. Wind erosion and volcanic activity contribute 40 to 50 percent of the atmospheric nickel from natural sources (ARB, 1991d).

AMBIENT CONCENTRATIONS

Nickel compounds are routinely monitored at the statewide ARB air toxics network. When nickel was formally identified as a toxic air contaminant, the ARB estimated a population-weighted annual concentration of 7.3 nanograms per cubic meter (ng/m^3) (ARB, 1991d). The network's mean concentration of nickel compounds from January 1996 through December 1996 is estimated to be 3.6 ng/m^3 (ARB, 1997c).

The United States Environmental Protection Agency (U.S. EPA) has also reported concentrations of nickel from 3 study areas during 1985. The overall range of concentrations from these areas was from 2.0 to 8.7 ng/m^3 with a mean concentration of 3.8 ng/m^3 (U.S. EPA, 1993a).

INDOOR SOURCES AND CONCENTRATIONS

Tobacco smoking is the major source of nickel in indoor air. Although further testing is necessary to determine the exact contribution tobacco smoking makes to indoor air concentrations of nickel, it is known that a single cigarette contains 1-3 micrograms (μg) of nickel and that a portion of that nickel becomes entrained during smoking (ARB, 1991d).

The amount of indoor air nickel from the burning of home heating and cooking fuels in California has not been determined. Other sources of indoor nickel emissions include house dust and the use of consumer products containing nickel. (U.S. EPA, 1986).

In a field study conducted in southern California, investigators collected particles (PM_{10}) inside 178 homes and analyzed the particle samples for selected elements, including nickel. Two consecutive 12-hour samples were collected inside and immediately outside each home. Nickel was present in measurable amounts in less than 10 percent of the indoor or outdoor samples (Pellizzari et al., 1992).

A study conducted by the South Coast Air Quality Management District showed that an average in-vehicle concentration for nickel is 9.0 ng/m^3 (Shikiya et al., 1989; ARB, 1991d).

ATMOSPHERIC PERSISTENCE

The atmospheric half-life and lifetime of nickel compounds is estimated to be 3.5 to 10 days and 5 to 15 days, respectively (Balkanski et al., 1993). Nickel particulate is removed from the atmosphere by either wet or dry deposition. The nickel associated with atmospheric pollutants is almost always detected in particulate matter. Nickel is continuously transferred among air, water, and soil by natural chemical and physical processes such as weathering, erosion, runoff, precipitation, and stream and river flow (ARB, 1991d).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics "Hot Spots" Program (AB 2588). Of the risk assessments reviewed as of April 1996, nickel and nickel compounds represented the principal cancer risk driver in 22 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million and contributed to the total cancer risk in 230 of these risk assessments. Nickel and nickel compounds also were the major contributors to the overall cancer risk in 5 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10

in 1 million, and contributed to the total cancer risk in 78 of these risk assessments (OEHHA, 1996a).

For non-cancer health effects, nickel and nickel compounds contributed to the total hazard index in 41 of the approximately 89 risk assessments reporting a total chronic hazard index greater than 1, and contributed to an individual hazard index greater than 1 in 2 of these risk assessments. Nickel and nickel compounds also contributed to the total hazard index in 50 of the approximately 107 risk assessments reporting a total acute hazard index greater than 1, and presented an individual hazard index greater than 1 in 31 of these risk assessments (OEHHA, 1996b).

HEALTH EFFECTS

Probable routes of human exposure to nickel are inhalation, ingestion, and dermal contact (U.S. EPA, 1994a).

Non-Cancer: The effects from long-term exposure to nickel include respiratory tract irritation and immune alterations such as dermatitis ("nickel itch") and asthma. Acute exposure to nickel and nickel compound fumes may cause irritation of the respiratory tract, skin, and eyes. A daily requirement of 50 μg of nickel has been estimated to be an essential element in human nutrition (U.S. EPA, 1994a). Nickel carbonyl is the most acutely toxic form of nickel. Exposure to nickel carbonyl can cause irritation of the lower respiratory tract and delayed pulmonary edema. It may also injure the liver and central nervous system (Olson, 1994).

An acute Reference Exposure Level (REL) of 1 microgram per cubic meter ($\mu g/m^3$) is listed for nickel compounds in the California Air Pollution Control Officers Association Air Toxics "Hot Spots" Program, Revised 1992 Risk Assessment Guidelines. The immune system is the toxicological endpoint considered for acute toxicity. A chronic non-cancer REL of 0.24 $\mu g/m^3$ for nickel and nickel compounds is also listed. The toxicological endpoint considered for chronic toxicity is the kidney, respiratory, and immune systems (CAPCOA, 1993). The U.S. EPA has not established a Reference Concentration (RfC) for nickel compounds but has determined an oral Reference Dose (RfD) for nickel (soluble salts) of 0.02 milligrams per kilogram per day based on decreased body and organ weights in rats. The U.S. EPA estimates that consumption of this dose or less, over a lifetime, would not likely result in the occurrence of chronic, non-cancer effects (U.S. EPA, 1994a).

The average daily intake of nickel is approximately 155 nanograms. Although there are insufficient data to assess nickel's effect on reproductive functions in humans, all forms of nickel examined to date in laboratory animals have exhibited adverse effects on male reproductive function. Animal studies also demonstrate that nickel adversely affects spermatogenesis, litter size and pup body weight, however, no teratogenic effects have been clearly demonstrated for compounds other than nickel carbonyl (ARB, 1991d). The State of California has determined under Proposition 65 that nickel carbonyl is a developmental toxicant (CCR, 1996).

Cancer: Inhalation exposure to nickel refinery dust and nickel subsulfide has been shown to cause nasal and lung cancer in refinery workers. The U.S. EPA has classified nickel refinery dusts and nickel subsulfide in Group A: Human carcinogen with an inhalation unit risk estimate of 2.4 x 10^{-4} (microgram per cubic meter)$^{-1}$ for nickel refinery dusts, and 4.8 x 10^{-4} (microgram per cubic meter)$^{-1}$ for nickel subsulfide. The U.S. EPA estimates that if an individual were to breathe air containing nickel refinery dusts at 0.004 $\mu g/m^3$, or air containing nickel subsulfide at 0.002 $\mu g/m^3$, over a lifetime, that person would theoretically have no more than a 1 in 1 million increased chance of developing cancer. Nickel carbonyl has been reported to cause lung tumors in animal studies. The U.S. EPA has classified nickel carbonyl in Group B2: Probable human carcinogen (U.S. EPA, 1994a).

The International Agency for Research on Cancer (IARC) reviewed nickel and nickel compounds in 1990 and concluded that there is sufficient evidence in humans for the carcinogenicity of nickel sulfate, and of the combinations of nickel sulfides and oxides encountered in the nickel refining industry; there is inadequate evidence in humans for the carcinogenicity of metallic nickel and nickel alloys; there is sufficient evidence in experimental animals for the carcinogenicity of metallic nickel, nickel monoxides, nickel hydroxides and crystalline nickel sulfides; there is limited evidence in experimental animals for the carcinogenicity of nickel alloys, nickelocene, nickel carbonyl, nickel salts, nickel arsenides, nickel antimonide, nickel selenides, and nickel telluride; and there is inadequate evidence in experimental animals for the carcinogenicity of nickel trioxide, amorphous nickel sulfide and nickel titanate. The IARC concluded that nickel compounds are carcinogenic to humans, classifying them in Group 1: Human carcinogen; and classified metallic nickel in Group 2B: Possible human carcinogen (IARC, 1990).

The International Committee on Nickel Carcinogenesis in Man indicated that the epidemiological evidence points to insoluble and soluble nickel compounds as contributing to the cancers seen in occupationally exposed persons. Both insoluble and soluble nickel compounds have produced tumors in animals by a variety of routes, primarily by injection. Both soluble and insoluble nickel compounds are genotoxic in a wide variety of assays. Evidence is available indicating that the Ni^{2+} ion is probably the carcinogenic agent (ICNCM, 1990).

The State of California under Proposition 65 and AB 1807 has determined that nickel and certain nickel compounds (nickel carbonyl, nickel refinery dust from the pyrometallurgical process, nickel subsulfide) are carcinogens (CCR, 1996; ARB, 1991d). The OEHHA staff concluded that based on available genotoxicity and carcinogenicity data and physiochemical properties of nickel compounds, all nickel compounds should be considered potentially carcinogenic to humans by inhalation, and total nickel should be considered when evaluating the risk by inhalation (ARB, 1991d). The inhalation potency factor that has been used as a basis for regulatory action in California is 2.6 x 10^{-4} (microgram per cubic meter)$^{-1}$ (OEHHA, 1994). In other words, the potential excess cancer risk for a person exposed over a lifetime to 1 $\mu g/m^3$ of nickel is estimated to be no greater than 260 in 1 million.

TABLE I - PHYSICAL PROPERTIES OF NICKEL AND NICKEL COMPOUNDS

Molecular Formula & Substance Name	CAS Registry Number & Synonyms	Color, Crystalline Form	Molecular Weight	Density	Melting Point (°C)	Boiling Point (°C)	Vapor Pressure	Solubility in 100 parts water
Ni nickel	7440-02-0	silver, face-centered	58.71	---	1455	2920	1 mm Hg at 1810 °C	insoluble; soluble in dilute HNO_3
$Ni(C_2H_3O_2)_2 \cdot 4H_2O$ nickel acetate tetrahydrate	6018-89-9	green pyramidal	248.86	1.74	decomposes at 250	----	----	16; soluble in alcohol
$Ni_3(AsO_4)_2$ nickel ortho-arsenate	---	yellow-green powder	453.97	4.98	----	----	----	insoluble
$Ni(BrO_3)_2 \cdot 6H_2O$ nickel bromate hexahydrate	---	green monoclinic	422.62	2.6	----	----	----	28 (20 °C)
$NiCO_3$ nickel carbonate	3333-67-3 nickelous carbonate	light green rhrombic	118.72	----	decomposes	----	----	0.009 (25 °C)
$NiCO_3 \cdot 2Ni(OH)_2$ nickel carbonate hydroxide	12607-70-4	green cubic	304.17	2.6	----	----	----	insoluble
C_4NiO_4 nickel carbonyl	13463-39-3 nickel tetracarbonyl	colorless liquid	170.75	1.32	-19.3	43	400 mm Hg at 25.8 °C	insoluble in alcohol
$NiCl_2$ nickel chloride	7718-54-9 nickelous chloride	yellow deliquescent	129.62	3.55	1030	sublimes at 970	----	60.8 (20°C)
NiF_2 nickel fluoride	10028-18-9 nickelous fluoride	yellow-green tetragonal	96.71	4.72	1450	1740	----	2.56 (20 °C)
$Ni(OH)_2 \cdot H_2O$ nickel hydroxide (hydrate)	---	green powder	110.74	----	decomposes 230	----	----	solubility 0.0013 (20 °C)
$Ni(NO_3)_2 \cdot 6H_2O$ nickel nitrate hexahydrate	13478-00-7 nickel(2+)nitrate, hexahydrate	green monoclinic deliquescent	290.81	2.05	56.7	137	----	150 (20°C)
NiO nickel oxide	1313-99-1 nickel monoxide	green cubic	74.71	7.45	2090	----	----	insoluble; soluble in acid
$NiSO_4 \cdot 6H_2O$ nickel sulfate hexahydrate	10101-97-0 nickel monosulfate hexahydrate	α blue-green tetragonal β green monoclinic	262.86	2.07	53.3 (forms β) loses H_2O at 280	----	----	40.1 (20 °C) 44.1 (20 °C)
Ni_3S_2 nickel subsulfide	12035-72-2 heazlewoodite	light yellow cubic	240.26	5.82	790	----	----	insoluble; soluble in HNO_3

(ARB, 1991)